Available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/watres

Adsorption of 2,4,6-trichlorophenol by multi-walled carbon nanotubes as affected by Cu(II)

Guang-Cai Chen^{a,b}, Xiao-Quan Shan^{a,*}, Yu-Sheng Wang^a, Bei Wen^a, Zhi-Guo Pei^a,
Ya-Ning Xie^c, Tao Liu^c, Joseph J. Pignatello^d

^aState Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China

^bResearch Institute of Subtropical Forestry, Chinese Academy of Forestry, Fuyang, Zhejiang 311400, China

^cBeijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

^dDepartment of Soil and Water, Connecticut Agricultural Experiment Station, 123 Huntington Street, New Haven, CT 06504-1106, USA

ARTICLE INFO

Article history:

Received 17 November 2008

Received in revised form

27 February 2009

Accepted 2 March 2009

Published online 11 March 2009

Keywords:

2,4,6-Trichlorophenol

Cu(II)

Multi-walled carbon nanotubes

Adsorption

ABSTRACT

Adsorption equilibrium of 2,4,6-trichlorophenol (TCP) on multi-walled carbon nanotubes (MWCNTs) was investigated to explore the possibility of using MWCNTs for concentration, detection and removal of TCP from contaminated water. The adsorption of TCP on MWCNTs at pH 4 was nonlinear, reversible and best fit by a Polanyi–Manes model. Oxidation treatment increased surface area and introduced hydrophilic carboxylic groups to the defect sites of MWCNTs, hence increased the sorption of TCP and Cu(II) individually. Cu(II) suppressed the sorption of TCP on oxidized MWCNTs15A, but had little effect on as-grown MWCNTs15. TCP had no influence on Cu(II) sorption to either. The mechanisms of Cu(II) suppression effect on TCP adsorption are ascribed to the formation of surface complexes of Cu(II), which was verified by X-ray absorption spectroscopy. Cu(II) exerts a cross-linking effect of functional groups on adjacent tubes, creating a more tightly knit bundle and suppressing the condensation of TCP in the pore spaces between the tubes. The large hydration sphere around surface complexes of Cu(II) may also intrude or shield hydrophilic sites, leading to the “crowding out” of TCP around the Cu(II)-complexed sites.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) are considered to be superior adsorbents of pollutants due to their unique properties and relative high reactivity. Their high adsorption capacities on removal of heavy metals (Li et al., 2002, 2003a; Lu and Chiu, 2006; Wang et al., 2005) and toxic organic chemicals (Chin et al., 2007; Long and Yang, 2001; Lu et al., 2005; Yang et al., 2006a,b; Yang and Xing, 2007) from water have been proved extensively.

The sorption capacity of CNTs can be modified by oxidative treatment with NaOCl, H₂O₂, KMnO₄ or HNO₃ (Li et al., 2003a; Lu

and Chiu, 2006; Wang et al., 2005). Oxidation removes impurities and hemispherical caps, hence increases surface area and introduces oxygen-containing functional groups (Li et al., 2003a; Lu and Chiu, 2006; Wang et al., 2005). Modification of the structure and surface properties of CNTs affected sorption capacity and sorption mechanisms of metals and organic chemicals (Li et al., 2003a; Lu and Chiu, 2006; Wang et al., 2005; Lu et al., 2005; Chin et al., 2007; Cho et al., 2008). The adsorption capacity of Cu²⁺ at a given pH followed the order NaOCl-modified CNTs > HNO₃-modified CNTs > as-produced CNTs (Wu, 2007). The extraordinary increase in sorption capacity and decrease in desorption rate of ²⁴³Am(III) after oxidation of

* Corresponding author. Tel.: +86 10 62923560; fax: +86 10 62923563.

E-mail address: xiaoquan@rcees.ac.cn (X.-Q. Shan).

0043-1354/\$ – see front matter © 2009 Elsevier Ltd. All rights reserved.

doi:10.1016/j.watres.2009.03.002

Table 1 – Selected structural properties of MWCNTs.

Carbons	Outer diameter (nm)	Inner diameter (nm)	Length (μm)	Purity (%)	A_{surf} ($\text{m}^2 \text{g}^{-1}$)	V_{meso} (cc g^{-1})	V_{micro} (cc g^{-1})	Oxygen content (atom %)
MWCNTs8	<8	2–5	10–30	95+	559	1.69	0.085	ND
MWCNTs15A	10–15	5–8	10–30	95+	279	0.57	0.026	3.92
MWCNTs15	10–15	5–8	10–30	90+	181	0.41	0.016	1.52
MWCNTs20	10–20	5–10	10–30	95+	167	0.55	0.016	ND
MWCNTs30	30–50	5–15	10–20	95+	91	0.30	ND ^a	ND
MWCNTs50	>50	5–15	10–20	95+	68	0.16	ND	ND

a ND, Not detected.

multi-walled carbon nanotubes (MWCNTs) suggested that chemisorption rather than physisorption and/or ion-exchange is the main sorption mechanism (Wang et al., 2005). The modified MWCNTs have different adsorption affinities for different metal ions, a study on the individual and competitive adsorption capacities of Pb^{2+} , Cu^{2+} and Cd^{2+} showed the adsorption affinity in the order of $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ (Li et al., 2003b). Nitric acid treatment of single-walled carbon nanotubes (SWCNTs) increased sorption of *p*-xylene, while it decreased sorption of *o*-xylene, suggesting that sorption depends on the substitution pattern on the ring and the density of oxygen-containing groups on the surface (Chin et al., 2007). Adsorption of naphthalene to MWCNTs decreased linearly with surface O content (Cho et al., 2008). X-ray photoelectron spectroscopy showed clearly that tetracene and phenanthrene molecules efficiently coated the external surface of SWCNTs. The adsorption of tetracene and phenanthrene caused a significantly higher frequency shift in radial breathing mode of the Raman spectrum of SWCNTs, indicating face-to-face adsorption with an intensive π – π interaction between these polycyclic aromatic hydrocarbons (PAHs) and SWCNTs (Gotovac et al., 2007).

Most research on sorption of metals or organic compounds by CNTs has been on single-solute systems. However, contaminants often exist in mixtures in the environment, where they may affect each other's sorption. Heavy metals and organic contaminants coexist at many contaminated sites (Dai et al., 2007; Sprovieri et al., 2007), and coexisting

heavy metal ions affect the adsorption of organic contaminants to soil, peat and charcoal (Pei et al., 2006, 2007; Chen et al., 2007). A few studies have been reported on competitive sorption between metals (Li et al., 2003b) or between organic contaminants on CNTs (Yang et al., 2006b).

Chlorinated phenols, including 2,4,6-trichlorophenol (TCP), have been widely used in agriculture, wood preservation, and pulp bleaching (Makinen et al., 1993; Suntio et al., 1988; Yoshida et al., 1987). They are found in the emissions from fossil fuel combustion, municipal waste incineration, and chlorination of water containing phenol or certain aromatic acids with hypochlorite or during disinfection of water (Chaliha and Bhattacharyya, 2008). TCP has been listed as a priority pollutant by the USEPA (Keith and Telliard, 1979) and China (Zhou et al., 1991) due to its animal carcinogenicity (NCI, 1979), producing lymphomas, leukemia, and liver cancer via oral exposure through drinking water or food. Copper is an essential element for life at low concentration, but is toxic at high concentration. It commonly exists in the soil environment, especially in soil irrigated by wastewater in countries with high water shortage. It should be realized that copper and TCP may occur together in field irrigated by wastewater and ground water (Daughney and Fein, 1997; Mueller et al., 1989). Coexistence of copper and TCP may affect their fates in the environment, but little is known on how they interact with each other on MWCNTs.

The aim of this study was to investigate the effect of copper on the sorption of TCP and vice versa on MWCNTs. Raman, Fourier transform infrared (FTIR) and X-ray absorption spectroscopy (XAS) studies were used to probe structure, surface functional groups and coordination environments of copper on MWCNTs in order to reveal the mechanism of copper–TCP interactions on the surface of MWCNTs.

Fig. 1 – Raman spectra of MWCNTs15A (a) and MWCNTs15 (b).

2. Experimental

2.1. Materials

TCP (>98%) was purchased from Aldrich Chemical Co. Inc. TCP has a $\log K_{ow}$ of 3.67, pK_a of 6.1 and a water solubility C_s of 300 mg L^{-1} ($\text{pH} < 5$) (Wightman and Fein, 1999). $\text{Cu}(\text{NO}_3)_2$ is of guaranteed reagent grade. Other chemicals are of analytical reagent grade or better.

MWCNTs with different diameters were purchased from Chengdu Organic Chemistry Co. Ltd, Chinese Academy of

Fig. 2 – FTIR spectra of MWCNTs15A (a) and MWCNTs15 (b).

Sciences. The numbers after MWCNTs in Table 1 are their outer diameters. These MWCNTs were synthesized from ethylene/nitrogen ($C_2H_4/N_2 = 3/2$) mixture by chemical vapor deposition at 823 K using Fe/Al_2O_3 as catalyst. MWCNTs15A refers to the material obtained after treating MWCNTs15 with 3 M nitric acid to remove impurities and hemispherical caps (Rinzler et al., 1998). The mixture of 2 g as-grown MWCNTs and 400 mL 3 M nitric acid was ultrasonically stirred for 24 hours. The suspension was filtrated and then rinsed with deionized water until the pH of the suspension reached about 6 and then was dried at 80 °C (Rinzler et al., 1998; Wang et al., 2005).

The diameters of MWCNTs were determined by TEM. The surface area and pore volume were measured by nitrogen gas adsorption and desorption at 77 K with ASAP2000 (Micromeritics Instrument Corporation), which were calculated by multi-point BET, BJH, and DR methods, respectively. The micropore volume was measured by carbon dioxide sorption with Quantachrome Instruments v2.2 and calculated with DFT method.

2.2. Batch adsorption experiments

Ten milligrams of MWCNTs were used for the sorption of TCP or Cu(II), while 20 mg of MWCNTs were used for the co-adsorption of Cu(II) and TCP. MWCNTs were combined with the test solute(s) dissolved in 20 mL deionized distilled water containing 0.01 mol L^{-1} $NaNO_3$ and 100 mg L^{-1} NaN_3 as a biocide in 40 mL screw-cap glass vials sealed with Teflon screw caps. All sorption experiments were performed in triplicate except for the sorption isotherms of TCP and sorption kinetics of Cu(II), which were conducted in duplicate. The pH was adjusted to 4 where dissolved TCP is predominantly (>99.3%) neutral, and where hydrolysis and precipitation of Cu(II) are negligible. This pH value is typical of the pH of red soil in southern China.

The vials were placed in a shaker at 20 ± 0.5 °C. Sorption of TCP on MWCNTs reaches apparent equilibrium within 24 hours. To be conservative, an equilibration time of 48 hours was used routinely. After sample centrifugation ($2000 \times g$ for 20 min), TCP in the liquid phase was determined by HPLC (HP 1100, Agilent Technologies) fitted with a diode array detector (DAD) at 220 nm, and an extended polar selectivity reversed-phase C18 column (15 cm $\times$ 4.6 mm i.d.). Isocratic elution was performed at a flow rate of 0.7 mL min^{-1} , the mobile phase was methanol/water (80%:20%). Cu(II) was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer) after filtration through a $0.45\text{-}\mu\text{m}$ hydrophilic polyethersulfone membrane. Blank experiments indicated that recoveries of adsorbates without MWCNTs added were greater than 97% of their initial concentrations, indicating no significant losses or degradation or adsorbed by the glass vials in the time frame of the batch sorption study. Therefore, the adsorbed mass was calculated by the difference between initial and final equilibrium concentrations.

2.3. XAS measurements and data analysis

The X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectra were collected at Beijing Synchrotron Radiation Facility on 4W1B beamline. Electron beam energy was 2.2 GeV with a storage ring beam current of 80 mA. Sample preparation and data collection followed the methods described in our

Fig. 3 – Deconvolution of the XPS C1s (a) and O1s (b) peaks of MWCNTs15A.

Fig. 4 – Effects of contact time (a, 10 mg of MWCNTs and 120 mg L⁻¹ of TCP in 20 mL of 0.01 M NaNO₃ at pH 4) and pH (b, 10 mg of MWCNTs and 120 mg L⁻¹ of TCP in 20 mL of 0.01 M NaNO₃ react for 48 hours) on the sorption of TCP by MWCNTs15A and MWCNTs15.

previous research (Pei et al., 2006). Briefly, data analysis was performed with WinXAS2.1 following background correction and normalization, Cubic spline, Fourier transformation and reverse Fourier transformation, and EXAFS fitting. In the fitting procedure, the coordination number was fixed for the reference compounds, while the Debye–Waller factor was fixed for samples. Phase shifts and backscattering amplitudes were obtained from the theoretical calculation using FEFF 7.0.

3. Results and discussion

3.1. Characterizations of MWCNTs

Selected structural properties of MWCNTs are listed in Table 1. MWCNTs15A, the product of nitric acid treatment of MWCNTs15, has a larger surface area and mesopore volume than MWCNTs15 due to the removal of amorphous carbon

and hemispherical caps on the nanotubes (Li et al., 2002, 2003a; Ying et al., 2003).

Raman spectra of MWCNTs15 and MWCNTs15A (Fig. 1) show three characteristic peaks at around 1585 cm⁻¹ (G band), 1333 cm⁻¹ (D band) and 1614 cm⁻¹ (D' band). The G band originates from in-plane tangential stretching of the carbon–carbon bonds in graphene sheets. The D band is due to defect sites in the hexagonal framework of walls of MWCNTs (Ying et al., 2003). The D' band, which is a weak shoulder of the G band, is induced by disorder and defects. Defect content is given by the ratio of D band to G band intensities (ID/IG). Nitric acid oxidative treatment increased ID/IG from 1.23 for MWCNTs15 to 1.68 for MWCNTs15A by eliminating amorphous carbon and modifying the outermost graphene layer of MWCNTs chemically. This finding is consistent with the results of Datsyuk et al. (2008) and Hsin et al. (2006).

The FTIR spectrum of MWCNTs15A (Fig. 2a) exhibits peaks at 1200 cm⁻¹ (C–N stretch) resulting from 3 M nitric acid treatment, 1570 cm⁻¹ (asymmetric –COO– stretch), 1720 cm⁻¹ (C=O stretch of keto or carboxyl groups), consistent with the results of Kim et al. (2007). It should be mentioned that the band at 1200 cm⁻¹ can be referred to the symmetric strength vibration (–COO–) as well. Consistently a band at 1570 cm⁻¹ appears in the FTIR, which is the asymmetric strength vibration (–COO–) (Schierz and Zanker, 2009). The spectrum of MWCNTs15 (Fig. 2b) shows a small peak at 1540 cm⁻¹. The FTIR spectra indicate that nitric acid treatment introduced more oxygen-containing functional groups (Coleman et al., 2003; Wang et al., 2005) on the outermost surface and defect sites that increase the hydrophilicity of MWCNTs. In this case, the oxidative treatment not only “attacks” the carbon defect sites but also creates additional defects (Datsyuk et al., 2008).

X-ray photoelectron spectroscopy (XPS) also provides useful information on the nature of functional groups and also on the presence of defects on the nanotube surface. In Fig. 3, the XPS C1s and O1s peaks of MWCNTs15A are presented. Deconvolution of the C1s peak (Fig. 3a) resolved a main peak of

Fig. 5 – Fit of PMM to the sorption of TCP onto six MWCNTs.

Table 2 – Nonlinear sorption isotherm models.

Model	Equation	Capacity term ^a
Freundlich model	$q_e = K_F C_e^N$	K_F ($\text{mg}^{1-N} \text{g}^{-1} \text{L}^{-N}$), Freundlich affinity coefficient; N , Freundlich exponential coefficient
Langmuir model	$q_e = Q^0 b C_e / (1 + b C_e)$	b (L mg^{-1}), Langmuir constants
Dual mode model	$q_e = Q^0 b C_e / (1 + b C_e) + K_P C_e$	K_P (L g^{-1}), partition coefficient
Dual Langmuir model	$q_e = Q_1^0 b_1 C_e / (1 + b_1 C_e) + Q_2^0 b_2 C_e / (1 + b_2 C_e)$	Q_1^0 (mg g^{-1}) and Q_2^0 (mg g^{-1}), sorbed capacity of site populations 1 and 2, respectively; b_1 and b_2 (L mg^{-1}), affinity coefficient of site populations 1 and 2, respectively
Polanyi–Manes model	$\log q_e = \log Q^0 + a(\varepsilon_{sw}/V_s)^b$ $\varepsilon_{sw} = RT \ln(C_s/C_e)$ or $q_e = Q^0 \text{EXP}(a^*(\varepsilon_{sw}/V_s)^b)$	ε_{sw} (kJ mol^{-1}), effective adsorption potential; V_s ($\text{cm}^3 \text{mol}^{-1}$), molar volume of solute; a ($(\text{cm}^3)^{b+1}(\text{kgJ})^{-b}$) and b , fitting parameters; R ($8.314 \times 10^{-3} \text{ kJ (mol K)}^{-1}$), universal gas constant; T (K), absolute temperature potential

a q_e (mg g^{-1}), equilibrium sorbed concentration; C_e (mg L^{-1}), equilibrium solution phase concentration; Q^0 (mg g^{-1}), sorbed capacity; C_s (mg L^{-1}), aqueous water solubility.

$\text{sp}^2 \text{C}=\text{C}$ (284.65 eV), attributed to the graphitic structure and a peak of $\text{sp}^3 \text{C}-\text{C}$ (285.4 eV) attributed to defects in the nanotube structure. Peaks of $\text{C}-\text{O}$ (288.6 eV), $>\text{C}=\text{O}$ (286.6 eV), and $\text{O}-\text{COO}$ (290.9 eV) were assigned to carbon atoms attached to different oxygen-containing moieties. Deconvolution of the XPS O1s peak (Fig. 3b) confirmed the presence of $\text{C}-\text{O}-\text{C}$, $\text{C}-\text{O}$, $\text{C}-\text{OH}$ at ~ 533.7 eV ($\text{C}-\text{O}-\text{C}$, $\text{C}-\text{O}$, $\text{C}-\text{OH}$), $\text{C}=\text{O}$, $\text{O}-\text{C}=\text{O}$ at ~ 532.3 eV, isolated $-\text{OH}$, $\text{C}=\text{O}$, $\text{O}-\text{C}=\text{O}$ at ~ 531.3 eV and O-physically absorbed, or carbonates at ~ 530.3 eV (Datsyuk et al., 2008).

3.2. Adsorption of TCP

The effects of contact time and pH on the sorption of TCP are given in Fig. 4. The sorption of TCP is very fast in the first 1 hour and reaches apparent equilibrium within 24 hours (Fig. 4a). The sorption of TCP is pH dependent. Sorption is approximately constant over the pH range of 3–5 and then declines in the pH range of 5–8 as TCP becomes ionized (Fig. 4b). Considering the pK_a value of 6.1 (Wightman and Fein, 1999) for TCP, it appears that the greater sorption at low pH 3–5 may be due to the predominant species of neutral TCP. An increase of solution pH value of 5–8 increased the fraction of negatively charged TCP species and the dissociation of functional groups of adsorbents (Pei et al., 2007; Wu, 2007). Therefore, the repulsion of anionic TCP with the negatively charged surfaces of MWCNTs makes sorption unfavorable. Furthermore, solubility of TCP increases rapidly with pH

above 6 (Wightman and Fein, 1999). The increase in solubility decreases the driving force for sorption of TCP on MWCNTs.

There are some differences in the adsorbed TCP between MWCNTs15A and MWCNTs15 as affected by contact time and pH (the inset of Fig. 4a and b). The modified MWCNTs15A is more hydrophilic and hardly amenable for organic substances, thus less TCP sorption onto MWCNTs15A is expected (Cho et al., 2008). However, oxidation treatment also increased the surface area and V_{meso} (Table 1), leading to the increased sorption of TCP. Overall, MWCNTs15A has higher adsorption affinity for TCP than does MWCNTs15 (Fig. 4).

The single-solute sorption isotherms of TCP at pH 4 are shown in Fig. 5. Five nonlinear sorption isotherm models (Table 2) of Freundlich (FM) (Freundlich, 1906), Langmuir (LM) (Langmuir, 1916), Dual Mode (DMM) (Xing and Pignatello, 1997), Dual Langmuir (DLM) (Sander and Pignatello, 2005) and Polanyi–Manes models (PMM) (Manes, 1980) were tested to fit the sorption of TCP on six MWCNTs. The PMM model fits all of the sorption isotherms well with the lowest MWSE (Fig. 5, Table 3). Other models were tested and rejected for the following reasons, FM and LM models failed to adequately describe the isotherms and greatly underestimated q at low equilibrium concentration (C_e), DMM and DLM models fit the isotherms well in most cases with the exception of lower concentration end of the isotherms of MWCNTs8 and MWCNTs15A (Fig. S1, Supporting information). Hence the following discussion is based on the adsorption parameters calculated from PMM fitting.

Table 3 – Results of PMM fit to the sorption isotherms of TCP on MWCNTs.

	$\log Q^0$ (mg g^{-1})	a [$(\text{cm}^3)^{b+1}(\text{kgJ})^{-b}$]	b	MWSE ^a	R^2	n
MWCNTs8	2.26 (0.04)	$-4.60\text{E}+06(1.61\text{E}+05)$	7.80 (1.36)	0.03	0.98	12
MWCNTs20	1.88 (0.03)	$-7.79\text{E}+01(1.07\text{E}+01)$	2.20 (0.36)	0.01	0.98	12
MWCNTs30	1.75 (0.05)	$-2.34\text{E}+01(1.08\text{E}+01)$	1.65 (0.42)	0.01	0.96	12
MWCNTs50	1.60 (0.03)	$-3.35\text{E}+01(1.01\text{E}+01)$	1.85 (0.33)	0.01	0.98	12
MWCNTs15	1.93 (0.03)	$-3.74\text{E}+02(1.09\text{E}+01)$	2.87 (0.43)	0.01	0.98	12
MWCNTs15A	1.97 (0.03)	$-7.21\text{E}+03(1.56\text{E}+02)$	4.31 (0.81)	0.02	0.97	12

a MWSE is mean weighted square error, equal to $1/\nu \sum [(q_{\text{measured}} - q_{\text{model}})^2 / q_{\text{measured}}^2]$, where ν is the amount of freedom; $\nu = N - 3$ for PMM; data in parentheses represent standard deviation.

Fig. 6 – Plot of adsorption capacities obtained from PMM for TCP against surface area (a) and micropore volumes (b) of MWCNTs.

The PMM theory was developed to describe physical adsorption to microporous adsorbents and involved a pore filling mechanism and the concept of a variable adsorption potential in response to pore filling (Manes, 1980). This theory would appear to be applicable in this case since MWCNTs form bundles in aqueous media and the spaces between the tubes within the bundles can be regarded as pores, as other researchers have (Yang et al., 2006a; Pan et al., 2008). Polanyi theory is applicable for either pore filling or flat surface adsorption (Condon, 2000). Sorption of TCP correlates with both initial surface area and micropore volume of the degassed sample (Fig. 6). The molecular surface area-based value of Q^0 ($\text{m}^2 \text{g}^{-1}$), taking the molecular surface area of TCP to be $1.86 \text{ nm}^2 \text{ molecule}^{-1}$ (Smejtek et al., 1996), correlates strongly with A_{surf} giving a slope of about 1.56 (Fig. 6a). Likewise, the molecular volume-based value of Q^0 ($\text{cm}^3 \text{g}^{-1}$), taking the liquid density of TCP to be 1.4901 g cm^{-3} (Lide, 2004),

correlates well with V_{micro} giving a slope of about 0.997 (Fig. 6b). These results suggest that TCP was mainly adsorbed onto the surface and within the pores of MWCNTs bundles or aggregates which is consistent with previous reports (Yang and Xing, 2007; Pan et al., 2008).

Considering the sorption properties of the above MWCNTs we choose MWCNTs15 and MWCNTs15A to represent as-grown and nitric acid oxidation treated MWCNTs for a comparison study on Cu(II) effect on the sorption of TCP below.

3.3. Adsorption of Cu(II)

Adsorption of Cu(II) by MWCNTs15 and MWCNTs15A is very fast and increased with pH in the range pH 3–6 (Fig. 7). The increase of Cu(II) sorption can be ascribed to the ionizable surface charge of MWCNTs. The isoelectric point was 2.85 and

Fig. 7 – Effects of contact time (a, 10 mg of MWCNTs and 30 mg L^{-1} of Cu(II) in 20 mL of 0.01 M NaNO_3 at pH 5) and pH (10 mg of MWCNTs and 30 mg L^{-1} of Cu(II) in 20 mL of 0.01 M NaNO_3 react for 24 hours) on sorption of Cu(II) by MWCNTs15A and MWCNTs15 (the dashed line represents the hydrolysis and precipitation of Cu(II), which cannot reflect the real adsorption).

Fig. 8 – LM fit of sorption isotherms of Cu(II) on MWCNTs15A (a) and MWCNTs15 (b).

4.86 for nitric oxidized and as-grown MWCNTs, respectively (Wu, 2007), which suggests that the surfaces of oxidized and as-grown MWCNTs were negatively charged at solution pH > 2.85 and > 4.86. The negatively charged surfaces of MWCNTs favor the adsorption of Cu(II). The increased sorption of MWCNTs15A is larger than that of MWCNTs15 over the pH range of 3–5, which can also be ascribed to the lower isoelectric point. Over the pH range of 6–9, the adsorption increased rapidly due to the combined role of adsorption and precipitation (Li et al., 2003b). Over the pH range of 7–9, the precipitation of Cu(II) was dominated, making true adsorption studies impossible.

Adsorption isotherms of Cu(II) were constructed at pH 4 (Fig. 8). The isotherms were fit well by the LM and the fitting parameters are given in Table 4. This result is consistent with the studies on the sorption of Cu²⁺, Pb²⁺ and UO₂²⁺ by CNTs which can be described by Langmuir model (Wu, 2007; Li et al., 2002; Schierz and Zanker, 2009). The total determined oxygen contents of MWCNTs15A and MWCNTs15 by XPS were 3.92% and 1.52%, respectively, and the sorption capacities were 5.26 mg g⁻¹ and 2.35 mg g⁻¹, respectively, suggesting that the sorption capacities of MWCNTs15A and MWCNTs15 were roughly positively correlated with their total oxygen contents. These results implied that complexation of Cu(II) by oxygen-

containing groups on the outermost graphene surface and defect sites was main sorption mechanism of Cu(II).

3.4. XAS study of Cu(II) adsorption

The nitric acid oxidation treatment introduced oxygen-containing groups, mainly carboxylic groups, which increased the adsorption of Cu(II) via the formation of outer- and inner-sphere complexes. The coordination environment around adsorbed Cu(II) is revealed by XAS. As previously observed by Frenkel et al. (2000), XANES spectra of adsorbed Cu(II) show a very weak peak just before the edge jump corresponding to 1s → 3d (Fig. 9a and b). The pre-edge peak is sensitive to the presence of a center of symmetry, and its intensity increases with distortions that remove this center of symmetry. The first derivative of XANES shows two different inflections corresponding to derivative peaks at 8.979 (α peak) and 8.984 keV (β peak). The intensity of the α peak is influenced by the degree of axial distortion and the covalence of equatorial ligands bonded to Cu(II) ions (Hahn et al., 1982), thus providing information about the Cu(II) binding environment. The decreased α peak intensity for Cu(II)–MWCNTs15A compared to aqueous Cu(NO₃)₂ (the inset of Fig. 9b) suggests that the stronger field water molecules in the tetragonal plane exchanged with organic ligands (carboxylic and hydroxylic functions) from MWCNTs15A, and also suggests that adsorbed Cu(II) is sterically hindered due to its three-dimensional structure. When Cu(II) approaches, it cannot bind in the equatorial plane with the same degree of angular overlap as water.

Normalized k³-weighted EXAFS spectra of Cu(II)–MWCNTs15A and its corresponding radial structural function derived from Fourier transformation are presented in Fig. 9c and d. The strongest radial structural function derived from Fourier transformation of EXAFS spectra occurring at 1.53 Å corresponded to first Cu(II)–O shell

Table 4 – Results of LM fit to Cu(II) sorption isotherms by MWCNTs.

Carbons	TCP (mg L ⁻¹)	Q ⁰ (mg g ⁻¹)	b (L mg ⁻¹)	MWSE	R ²	n
MWCNTs15A	0	5.26	0.25	0.05	0.98	18
	50	5.35	0.21	0.05	0.98	18
MWCNTs15	0	2.35	0.04	0.04	0.98	18
	50	2.49	0.04	0.03	0.99	18

Fig. 9 – Normalized XANES spectra (a), corresponding first derivatives (b), EXAFS spectra (χ -function) (c), and Fourier transform of EXAFS (d) spectra of Cu(II)–MWCNTs15A (10 mg of MWCNTs15A and 65 mg L^{−1} of Cu(II) in 20 mL of 0.01 M NaNO₃ react for 24 hours at pH 4). Solid lines represent the experimental data and open circles correspond to the lines of best fitting.

(Fig. 9d). The best fit of this peak leads to 4.14 equatorial oxygen atoms at 1.94 Å, 2.64 axial oxygen atoms at 2.20 Å for Cu(II)–MWCNTs15A. The data are consistent with those obtained from XANES (i.e., a slightly distorted octahedral coordination around Cu(II) sorption onto MWCNTs15A) involving Cu(II) (Flogeac et al., 2004). The results of four short equatorial bonds and two elongated axial bonds were due to the Jahn–Teller effect of the Cu(II)–O clusters. The results suggest that Cu(II) complexes were formed on MWCNTs15A through carboxylic and hydroxylic groups.

The XAS spectra of MWCNTs15 were difficult to resolve due to the low concentration of adsorbed Cu(II) compared to MWCNTs15A.

3.5. Competitive sorption between Cu(II) and TCP

The effect of Cu(II) on TCP sorption was evaluated by adding TCP and various amounts of Cu(II) simultaneously to MWCNTs15A or MWCNTs15 suspensions at pH 4. Sorption of TCP by MWCNTs15A decreased markedly, while the sorption

Fig. 10 – Effect of Cu(II) on the sorption of TCP onto MMCNT15A (a) and MMCNT15 (b) (Symbols represent experimental data, and lines represent the fitting of PMM).

Table 5 – The K_d values ($L\ g^{-1}$) of TCP on MWCNTs as affected by Cu(II).^a

Initial concn. ($mg\ L^{-1}$)	MWCNTs15A			MWCNTs15		
	K_d^1	K_d^2	K_d^3	K_d^1	K_d^2	K_d^3
	Cu(II)	Cu(II)	Cu(II)	Cu(II)	Cu(II)	Cu(II)
	0	6.5 $mg\ L^{-1}$	65 $mg\ L^{-1}$	0	6.5 $mg\ L^{-1}$	65 $mg\ L^{-1}$
30	15.24	13.34	12.92	10.37	9.63	9.38
50	4.7	4.47	4.06	2.07	1.89	1.80
100	2.25	1.9	1.74	1.15	1.04	1.06
150	1.6	1.3	1.21	1.01	1.01	0.94
200	1.23	1.05	0.95	0.92	0.86	0.83
250	1.11	0.96	0.79	0.85	0.79	0.79

^a K_d is distribution coefficient, equal to q_e/C_e .

of TCP by MWCNTs15 was only slightly suppressed, if at all, when 6.5 or 65 $mg\ L^{-1}$ of Cu(II) were present (Fig. 10). In addition, competitive sorption was greater at higher than at lower TCP concentrations. The impact of Cu(II) on TCP sorption was expressed as $(K_d^2 - K_d^1)/K_d^1$, where K_d^2 and K_d^1 correspond to the distribution coefficients (equal to the ratio q_e/C_e) of TCP with and without Cu(II), respectively (Table 5). The presence of Cu(II) at concentrations of 6.5 $mg\ L^{-1}$ and 65 $mg\ L^{-1}$ decreased the sorption of TCP onto MWCNTs15A by 15% and 30%, respectively, and less than 10% onto MWCNTs15, respectively. In contrast, co-adsorption of TCP at concentration of 50 $mg\ L^{-1}$ had little effect on the sorption of Cu(II) on MWCNTs15 and MWCNTs15A (Fig. 8).

4. Conclusions

TCP may undergo both adsorption on MWCNT surfaces and condensation in the pore spaces within bundles of individual MWCNTs. This is supported by the application of PMM and strong correlation of sorption capacity with surface areas and pore volumes, as well as the results of other studies (Yang and Xing, 2007; Pan et al., 2008). It is widely known that CNTs unmodified with surfactants or covalently attached groups exist in a bundled state in water due to strong van der Waals interactions between the tubes. It is reasonable that TCP can be condensed in the pore spaces between tubes although no desorption hysteresis was observed (Fig. S2, Supporting information). As condensation progresses, TCP–CNT interactions compete with CNT–CNT interactions, causing the bundles to swell slightly and facilitating further condensation. Nitric acid treatment introduces hydrophilic functional groups that reduce CNT–CNT interactions. Copper acts by cross-linking functional groups on adjacent tubes, creating a more tightly knit bundle and suppressing condensation of TCP. Nitric acid treatment promotes competition with Cu(II) because it creates more cross-linking opportunities.

Furthermore, the suppression of TCP sorption by Cu(II) can be explained by assuming that Cu(II) forms strong outer- and inner-sphere complexes at hydrophilic defect sites (Fig. 9), which provide steric hindrance to TCP binding sites due to the sizable hydration sphere of adsorbed Cu(II). This “crowding out” hypothesis is supported by the results of Chen et al.

(2007) who found that Cu(II) suppresses sorption of both hydrogen bonding solutes (2,4-dichlorophenol) and apolar solutes (1,2-dichlorobenzene and naphthalene) on wood char, whose primary structure, analogous to CNTs with defects, is the graphene sheet rimmed by oxygen functional groups. Just as with CNTs, competition appears to be relatively greater at higher than at lower concentration of the principal solute (Chen et al., 2007).

Acknowledgments

This work was funded by the National Natural Science Foundation of China (grant number: 20707037) with further support from CSREES, U.S. Department of Agriculture.

Appendix. Supplementary data

Two figures (Fig. S1 – Fit of FM (a), LM (b), DMM (c) and DLM (d) to the sorption of TCP onto six MWCNTs; Fig. S2 – Effect of Cu(II) on the desorption of TCP from MWCNTs15A (a, without Cu(II) adsorbed; b, with 6.5 $mg\ L^{-1}$ Cu(II) simultaneously adsorbed) and MWCNTs15 (c, without Cu(II) adsorbed; d, with 6.5 $mg\ L^{-1}$ Cu(II) simultaneously adsorbed)).

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.watres.2009.03.002](https://doi.org/10.1016/j.watres.2009.03.002).

REFERENCES

- Chaliha, S., Bhattacharyya, K.G., 2008. Catalytic wet oxidation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in water with Mn(II)–MCM41. *Chemical Engineering Journal* 139, 575–588.
- Chen, J.Y., Zhu, D.Q., Sun, C., 2007. Effect of heavy metals on the sorption of hydrophobic organic compounds to wood charcoal. *Environmental Science and Technology* 41, 2536–2541.
- Chin, C.J.M., Shih, L.C., Tsai, H.J., Liu, T.K., 2007. Adsorption of o-xylene and p-xylene from water by SWCNTs. *Carbon* 45, 1254–1260.
- Cho, H., Smith, B.A., Wnuk, J.D., Fairbrother, D.H., Ball, W.P., 2008. Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes. *Environmental Science and Technology* 42, 2899–2905.
- Coleman, K.S., Bailey, S.R., Fogden, S., Green, M.L.H., 2003. Functionalization of single-walled carbon nanotubes via the Bingel reaction. *Journal of the American Chemical Society* 125, 8722–8723.
- Condon, J.B., 2000. Equivalency of the Dubinin–Polanyi equations and the QM based sorption isotherm equation. Part B. Simulations of heterogeneous surfaces. *Microporous and Mesoporous Materials* 38, 377–383.
- Dai, J.Y., Xu, M.Q., Chen, J.P., Yang, X.P., Ke, Z.S., 2007. PCDD/F, PAH and heavy metals in the sewage sludge from six wastewater treatment plants in Beijing, China. *Chemosphere* 66, 353–361.
- Datsyuk, V., Kalyva, M., Papagelis, K., Parthenios, J., Tasis, D., Siokou, A., Kallitsis, S.I., Galiotis, C., 2008. Chemical oxidation of multiwalled carbon nanotubes. *Carbon* 46, 833–840.

- Daughney, C.J., Fein, J.B., 1997. Aqueous complexation of cadmium, lead, and copper by 2,4,6-trichlorophenolate and pentachlorophenolate. *Geochimica et Cosmochimica Acta* 61, 719–729.
- Flogeac, K., Gullion, E., Aplincourt, M., 2004. Surface complexation of copper(II) on soil particles, EPR and XAFS studies. *Environmental Science and Technology* 38, 3098–3103.
- Freundlich, H.M.F., 1906. Over the adsorption in solution. *Journal of Physical Chemistry* 57, 385–470.
- Frenkel, A., Korshin, G.V., Ankudinov, A.L., 2000. XANES study of Cu^{2+} -binding sites in aquatic humic substances. *Environmental Science and Technology* 34, 2138–2142.
- Gotovac, S., Honda, H., Hattori, Y., Takahashi, K., Kanoh, H., Kaneko, K., 2007. Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons. *Nano Letters* 7, 583–587.
- Hahn, J.E., Scott, R.A., Hodgson, K.O., Doniach, S., Desjardins, S.R., Solomon, E.I., 1982. Observation of an electric quadrupole transition in the X-ray absorption spectrum of a Cu(II) complex. *Chemical Physics Letters* 88, 595–598.
- Hsin, Y.L., Lai, J.Y., Hwang, K.C., Lo, S.C., Chen, F.R., Kai, J.J., 2006. Rapid surface functionalization of iron-filled multi-walled carbon nanotubes. *Carbon* 44, 3328–3335.
- Keith, L.H., Telliard, W.A., 1979. ES&T special report: priority pollutants: part I – a perspective view. *Environmental Science and Technology* 13, 416–423.
- Kim, S.D., Kim, J.W., Im, J.S., Kim, Y.H., Lee, Y.S., 2007. Oxidation of multiwalled carbon nanotubes by nitric acid. *Journal of Fluorine Chemistry* 128, 60–64.
- Li, Y.H., Wang, S., Wei, J., Zhang, X., Luan, Z., Wu, D., Wei, B., 2002. Lead adsorption on carbon nanotubes. *Chemical Physics Letters* 357, 263–266.
- Li, Y.H., Wang, S., Luan, Z., Ding, J., Xu, C., Wu, D., 2003a. Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon* 41, 1057–1062.
- Li, Y.H., Ding, J., Luan, Z.K., Di, Z.C., Zhu, Y.F., Xu, C.L., Wu, D.H., Wei, B.O., 2003b. Competitive adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon* 41, 2787–2792.
- Lide, D.R., 2004. *Handbook of Chemistry and Physics*, eighty fifth ed. CRC Press, Boca Raton, FL.
- Langmuir, I., 1916. The adsorption of gases on plane surface of glass, mica and platinum. *Journal of the American Chemical Society* 40, 1361–1368.
- Long, R.Q., Yang, R.T., 2001. Carbon nanotubes as superior sorbent for dioxin removal. *Journal of the American Chemical Society* 123, 2058–2059.
- Lu, C., Chung, Y.L., Chang, K.F., 2005. Adsorption of trihalomethanes from water with carbon nanotubes. *Water Research* 39, 1183–1189.
- Lu, C., Chiu, H., 2006. Adsorption of zinc(II) from water with purified carbon nanotubes. *Chemical Engineering Science* 61, 1138–1145.
- Manes, M., 1980. The Polanyi adsorption potential theory and its application to adsorption from water solution onto activated carbon. In: Suffet, I.H., McGuire, M.J. (Eds.), *Activated Carbon Adsorption of Organics from the Aqueous Phase*. Ann Arbor Science, Michigan, pp. 43–63.
- Makinen, P.M., Theno, T.J., Ferguson, J.F., Ongerth, J.E., Puhakka, P.M., 1993. Chlorophenol toxicity removal and monitoring in aerobic treatment: recovery from process upsets. *Environmental Science and Technology* 27, 1434–1439.
- Mueller, J.G., Chapman, P.J., Pritchard, P.H., 1989. Creosote-contaminated sites. Their potential for bioremediation. *Environmental Science and Technology* 23, 1197–1201.
- NCI, 1979. Bioassay of 2,4,6-trichlorophenol for possible carcinogenicity (CAS No. 88-06-2), Technical Report Series No 155, DHEW (NIH) Publication No. 79-1711, National Institutes of Health, Bethesda, MD, pp. 131.
- Pan, B., Lin, D., Mashayekhi, H., Xing, B., 2008. Adsorption and hysteresis of bisphenol A and 17 α -ethinyl estradiol on carbon nanomaterials. *Environmental Science and Technology* 42, 5480–5485.
- Pei, Z.G., Shan, X.Q., Liu, T., Xie, Y.N., Wen, B., Zhang, S.Z., Khan, S.U., 2006. Sorption of *p*-nitrophenol on two Chinese soils as affected by copper. *Environmental Toxicology and Chemistry* 25, 2584–2592.
- Pei, Z.G., Shan, X.Q., Liu, T., Xie, Y.N., Wen, B., Zhang, S.Z., Khan, S.U., 2007. Effect of lead on the sorption of 2,4,6-trichlorophenol on soil and peat. *Environmental Pollution* 147, 764–770.
- Rinzler, A.G., Liu, J., Dai, H., Nikolaev, P., Huffman, C.B., Rodriguez-Macias, F.J., Boul, P.J., Lu, A.H., Heymann, D., Colbert, D.T., Lee, R.S., Fischer, J.E., Rao, A.M., Eklund, P.C., Smalley, R.E., 1998. Large-scale purification of single-wall carbon nanotubes, process, product, and characterization. *Applied Physics A* 67, 29–37.
- Sander, M., Pignatello, J.J., 2005. Characterization of charcoal adsorption sites for aromatic compounds: insights drawn from single-solute and bi-solute competitive experiments. *Environmental Science and Technology* 39, 1606–1615.
- Schierz, A., Zanker, H., 2009. Aqueous suspensions of carbon nanotubes: surface oxidation, colloidal stability and uranium sorption. *Environmental Pollution* 157, 1088–1094.
- Smejtek, P., Blochel, A., Wang, S., 1996. Hydrophobicity and sorption of chlorophenolates to lipid membranes. *Chemosphere* 33, 177–201.
- Sprovieri, M., Feo, M.L., Prevedello, L., Manta, D.S., Sammartino, S., Tamburrino, S., Marsella, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere* 67, 998–1009.
- Suntio, L.R., Shiu, W.Y., Mackay, D., 1988. A review of the nature and properties of chemicals present in pulp mill effluents. *Chemosphere* 17, 1249–1290.
- Wang, X.K., Chen, G., Hu, W., Ding, A., Xu, D., Zhou, X., 2005. Sorption of $^{243}\text{Am}(\text{III})$ to multiwall carbon nanotubes. *Environmental Science and Technology* 39, 2856–2860.
- Wightman, P., Fein, J.B., 1999. Experimental study of 2,4,6-trichlorophenol and pentachlorophenol solubilities in aqueous solutions: derivation of a speciation-based chlorophenol solubility model. *Applied Geochemistry* 14, 319–331.
- Wu, C.-H., 2007. Studies of the equilibrium and thermodynamics of the adsorption of Cu^{2+} onto as-produced and modified nanotubes. *Journal of Colloid and Interface Science* 311, 346–388.
- Xing, B.S., Pignatello, J.J., 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environmental Science and Technology* 31, 792–799.
- Yang, K., Zhu, L.Z., Xing, B.S., 2006a. Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environmental Science and Technology* 40, 1855–1861.
- Yang, K., Wang, X.L., Zhu, L.Z., Xing, B.S., 2006b. Competitive sorption of pyrene, phenanthrene, and naphthalene on multiwalled carbon nanotubes. *Environmental Science and Technology* 40, 5804–5810.
- Yang, K., Xing, B.S., 2007. Desorption of polycyclic aromatic hydrocarbons from carbon nanomaterials in water. *Environmental Pollution* 145, 529–537.
- Ying, Y.M., Saini, R.K., Liang, F., Sadana, A.K., Billups, W.E., 2003. Functionalization of carbon nanotubes by free radicals. *Organic Letters* 5, 1471–1473.
- Yoshida, K., Shigeoka, T., Yamamuchi, F., 1987. Evaluation of aquatic environmental fate of 2,4,6-trichlorophenol with a mathematical model. *Chemosphere* 16, 2531–2544.
- Zhou, W.M., Fu, D.Q., Sun, Z.G., 1991. Determination of black list of China's priority pollutants in water. *Research of Environmental Sciences* 4, 912–915.